The Nuclear Magnetic Resonance Spectra of Geometrical Isomers of 2,4-Difluoro-1,3-di-*t*-butylcyclodiphosph(III)azane

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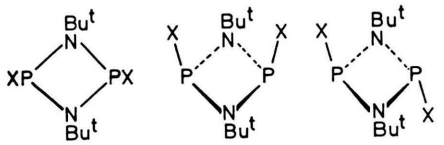
A new synthetic method for the preparation of the geometrical isomers of $(FPNBu^t)_2$ by amine elimination from $Me_2N–P(F)–NBu^tSiMe_2$ is described.

The ^{13}C, ^{19}F, and ^{31}P NMR investigations lead to new structural assignments.

Although alkyl [1], amino [2–4], and alkoxy [5] derivatives of cyclodiphosph(III)azanes (**1**) are often obtained as mixtures of *cis*- and *trans*-isomers, only one isomer of each of the halogeno derivatives (**1**) (X = F [6], Cl [7], and Br [8]) has been isolated.



1 **2** **3**

In the solid state (**1**) (X = Cl) has a *cis*-structure (**2**), and it has been assumed that the same structure is obtained for the analogous bromide, (**1**) (X = Br) [8].

It seems very likely that the *cis*-structures also exist in solution. In this connection, the ^{19}F and ^{31}P NMR data of the fluoride (**1**) (X = F) are particularly interesting, since the spectra constitute an example of an AA′XX′ spin system from which P···P, F···F and other spin couplings can, in principle, be obtained.

It has been suggested that the F···F coupling in particular reflects the geometrical arrangement of the fluorine atoms [9]. Spin couplings of *ca.* 95 and 30 Hz were first assigned to $^2J_{(PP')}$ and $^4J_{(FF')}$ respectively. Unfortunately, the analysis does not distinguish between $J_{(AA')}$ and $J_{(XX')}$, and the earlier assignment [5] was reversed as a result of comparisons with data obtained for other fluorocyclodiphosph(III)azanes. This revision is consistent with the finding [10] that $^4J_{(F_AF_B)}$ is also relatively large (53 Hz) in a platinum complex of (**1**) (X = F). The larger coupling has since been assigned to $^2J_{(PP')}$ but the authors [11] appeared to be unaware of previous work in the area.

It has now been found that a mixture of geometrical isomers (**2**) and (**3**) can be obtained by the following reaction sequence:

$$Me_2N–PF_2 + LiNBu^t(SiMe_3) \xrightarrow[120\ °C]{-LiF} Me_2N–P(F)–NBu^t(SiMe_3)\ \mathbf{4} \longrightarrow (FPNBu^t)_2 + Me_2NSiMe_3$$

(**4**)

2, **3**

The major isomer has ^{19}F and ^{31}P NMR shifts similar to those previously reported [6, 9]. On standing at ambient temperature the proportion of the major isomer slowly increased. The proton-decoupled ^{19}F and ^{31}P NMR spectra of both isomers were analysed and the results are shown in the Table.

It can be deduced by inspection that $^1J_{(PF)}$ (negative [12]) and $^3J_{(PF)}$ are of opposite sign in both isomers. The relative signs of $^2J_{(PP')} + {}^4J_{(FF')}$ and $^1J_{(PF)} + {}^3J_{(PF')}$ were established by a series of $^{31}P–\{^{19}F\}$ double resonance experiments. These experiment confirmed previous findings [9] for the major isomer (Table), and showed that these combinations of spin couplings were of opposite sign in the minor isomer. The combinations $|^2J_{(PP')} + {}^4J_{(FF')}|$ and $|^2J_{(PP')} - {}^4J_{(FF')}|$ could not be distinguished in the double resonance experiments on the minor isomer as the 1.0 Hz splitting that was observed in the ^{19}F spectrum was not resolved in the ^{31}P spectrum. Hence the sign of the smaller (1.0 Hz) coupling could not be obtained, although the 75.3 Hz coupling in the minor isomer was shown to be positive.

Comparison of ^{13}C and ^{31}P chemical shifts and PNC spin couplings for the two isomers with those of cyclodiphosph(III)azanes of known structure [1–5, 13, 14] are consistent with the assignment of a *cis*-structure to the isomer with δ_P 165.5 as in previous work. The fact that $^2J_{(PP')}$ is generally small (< 20 Hz) and negative for some *trans*-isomers of cyclodiphosph(III)azanes [9], indicates that the relatively large coupling of + 75.3 Hz must be assigned to $^4J_{(FF')}$. Thus $^4J_{(FF')}$ (= + 94.4 Hz) in the *cis*-isomer [2] is not necessarily dominated by a trough-space interaction [9]. Support for this viewpoint comes from the measurement of $^4J_{(FF)}$ in the *trans* (2-*trans*-4-*cis*-6) isomer of $(FPNEt)_3$ where these couplings all lie in the range 10–20 Hz [15].

There appears to be no doubt that the *cis*-isomer of these halogeno-cyclodiphosph(III)azanes are thermodynamically favoured over the analogous

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Table. ^{13}C, ^{19}F, and ^{31}P NMR data[a].

Compound	δ_P	δ_F	δ_{NC}	$^1J(PF)$	$^3J(PF')$	$^2J(PP')$	$^4J(FF')$	$^2J(PC)$
2 (X = F)	165.5	—23.2	51.6[b]	—1180.6	+ 22.1	+ 29.3	+ 94.0	9.6[d]
3 (X = F)	247.9	—36.4	51.5[c]	—1171.3	+ 20.7	1.0	+ 75.3	6.3[e]

[a] Obtained from $CDCl_3$ solutions at ambient temperature. References were TMS (^{13}C), CCl_3F (^{19}F), and H_3PO_4 (^{31}P); downfield shifts are positive. Spectra were obtained on a Varian XL-100 NMR spectrometer in the pulsed Fourier Transform mode, with proton-noise decoupling except for the ^{31}P–{^{19}F} double resonance experiments. Spin couplings are in Hz (for the AA'XX' spectra, measured from the ^{19}F NMR data). [b] δ_{NCC} = 30.7, $^3J(PC)$ = 5.9 Hz, $^4J(FC)$ = 1.0 Hz; [c] δ_{NCC} = 30.2, $^3J(PC)$ = 5.8 Hz, $^4J(FC)$ = 1.2 Hz; [d] $^3J(FC)$ = 1.2 Hz; [e] $^3J(FC)$ = 1.8 Hz.

trans-isomers. Whilst *cis*- and *trans*-isomers are expected to have puckered and planar ring, respectively [14], arguments relating ring conformations to thermodynamic stability are still rather speculative.

Experimental

The usual precautions in handling air and moisture sensitive compounds were observed.

I. N,N-t-butyl(trimethylsilyl)amino-N',N'-dimethylaminofluoro-phosphan (**4**)

49.8 g (330 mmoles) Lithium-*t*-butyl(trimethylsilyl)amide [16] in 200 ml diethylether were added slowly to 40.0 g (354 mmoles) N,N-dimethylaminodifluorophosphane [17] in 100 ml diethylether. After stirring under reflux (about 1 h) the solvent was evaporated. Vacuum distillation of the residue yields 54.2 g (69%) (**4**).

Calcd C45.34 H10.15 F7.97 N11.75 P12.99,
Found C46.08 H10.04 F8.30 N11.75 P13.48.

$\delta^{31}P$ 166.3, $^1J_{PF}$ 1042; $\delta^{19}F$ —92.1; $\delta^{29}Si$ 3.8, $^2J_{SiP}$ 9.5, $^3J_{SiF}$ 2.0; δ^1H (Me_2N) 2.57, $^3J_{HP}$ 8.9, $^4J_{HF}$ 4.50; (Me_3C) 1.35, $^4J_{HP}$ 1.80, $^5J_{HF}$ 0.62; (Me_3Si) 0.29, $^4J_{HP}$ 2.38, $^5J_{HF}$ 0.26.

IR ($1500 > \tilde{\nu} > 800$): 1481 m, 1450 m, 1401 m, 1392 m, 1362 st, 1278 m, 1265 sh, 1252 vst, 1191 vst, 1140 w, 1058 m, 947 st, 915 vst, 896 vst, 866 m, 843 vst, 825 sh cm^{-1}.

II. 2,4-Difluoro-1,3-di-t-butyl-cyclodiphosph(III)azanes (**2**, **3**)

23.8 g (100 mmoles) (**4**) were pyrolised 2 h at 110 °C. Volatile products were condensed (—78 °C) and sublimed again (40 °C/0.05 Torr). Yield: 4,8 g (40%).

Calcd C39.67 H7.49 F15.59 N11.57 P25.58,
Found C38.65 H7.93 F14.90 N10.67 P26.13.

MS: m/e = 242 M^+ (35%), 227 M^+–Me (94%) ... 106 Me_2NCNPF (100%) ...

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